

Journées scientifiques CenTRA 2024

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Batiment Principal



Recueil des résumés

X-RAY ABSORPTION SPECTROSCOPY
WITH APPLICATION TO RARE EARTHS

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In this presentation we shall give an introduction to the technique of X-ray absorption spectroscopy (XAS).

In a first step, we shall focus on the basic theoretical description of XAS with a specific attention dedicated to the selection rules and we shall also review the theoretical framework necessary for the description of the electronic structures of the rare earths in the context of XAS. Secondly, the instrumental technique will be shortly outlined to stress its potential. Thirdly, applications where the polarization of X-rays is used shall be detailed with specific attention to the magnetic properties of 4f elements, to crystal field effects, and to Kondo transitions. Finally, if time permitted we shall enlarge the picture to recent spectroscopic experiments on actinides.

25 ANS D'UTILISATION DE COMPLEXES DE LANTHANIDE POUR LA BIOLOGIE STRUCTURALE

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Au cours de cette présentation, j'exposerai les challenges passé, présent et futur associés à l'obtention d'information structurale sur des macromolécules biologiques. Je me focaliserai sur l'apport des complexes de lanthanide dans la levée de problématiques méthodologiques pour les deux techniques que sont la diffraction des rayons X, en particulier pour la production de cristaux de protéines, et la diffusion aux petits angles combinée à la variation de contraste. Enfin, à travers quelques exemples, je montrerai que ces études peuvent apporter un nouvel éclairage sur les propriétés d'interactions des complexes de lanthanide.

Sélection de Publications :

1. Girard, E., Chantalat, L., Vicat, J. & Kahn, R. Gd-HPDO3A, a complex to obtain high-phasing-power heavy-atom derivatives for SAD and MAD experiments: results with tetragonal hen egg-white lysozyme. *Acta Crystallogr D Biol Crystallogr* **58**, 1–9 (2002).
2. Girard, E., Stelter, M., Vicat, J. & Kahn, R. A new class of lanthanide complexes to obtain high-phasing-power heavy-atom derivatives for macromolecular crystallography. *Acta Crystallogr D Biol Crystallogr* **59**, 1914–1922 (2003).
3. Girard, E., Stelter, M., Anelli, P. L., Vicat, J. & Kahn, R. A new class of gadolinium complexes employed to obtain high-phasing-power heavy-atom derivatives: results from SAD experiments with hen egg-white lysozyme and urate oxidase from *Aspergillus flavus*. *Acta Crystallogr D Biol Crystallogr* **59**, 118–126 (2003).
4. Pompidor, G. *et al.* Protein crystallography through supramolecular interactions between a lanthanide complex and arginine. *Angewandte Chemie International Edition* **47**, 3388–3391 (2008).
5. Engilberge, S. *et al.* Crystallophore: a versatile lanthanide complex for protein crystallography combining nucleating effects, phasing properties, and luminescence. *Chem. Sci.* **8**, 5909–5917 (2017).
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SINGLE ERBIUM ION IN SCHEELITE MEASURED BY MICROWAVE PHOTON COUNTING.

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Electron spin resonance (ESR) spectroscopy is the method of choice for characterizing paramagnetic impurities, with applications ranging from chemistry to quantum computing, but it gives only access to ensemble-averaged quantities due to its limited signal-to-noise ratio. The sensitivity needed to detect single electron spins has been reached so far using spin-dependent photoluminescence, transport measurements, or scanning probes. These techniques are system-specific or sensitive only in a small detection volume, so that practical single spin detection remains an open challenge. Using single-electron-spin-resonance techniques recently demonstrated [3] we characterize the magnetic environment of the single electron probe. The technique consists in measuring the spin fluorescence signal at microwave frequencies [1, 2] using a microwave photon counter based on a superconducting transmon qubit [3]. In our experiment, individual paramagnetic erbium ions in a scheelite crystal of CaWO_4 are magnetically coupled to a small-mode-volume, high-quality factor superconducting microwave resonator to enhance their radiative decay rate [4]. The method applies to arbitrary paramagnetic species with long enough non-radiative relaxation time, and offers large detection volumes ($\sim 10\mu\text{m}^3$); as such, it may find applications in magnetic resonance and quantum computing.

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COMPORTEMENT CHIMIQUE DES ÉLÉMENTS 5f :

QUELQUES ILLUSTRATIONS

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Cette présentation sera l'occasion dans un premier temps de discuter des propriétés chimiques des éléments actinides (5f) les plus marquantes en solution aqueuse. Parmi celles-ci, le comportement rédox sera plus particulièrement abordé.

Dans une seconde étape, les grands axes de Recherche & Développement seront présentés, en se focalisant sur les éléments transuraniens ($Z > 92$).

Enfin, une cartographie des laboratoires développant des travaux avec les actinides sera proposée. Cette cartographie sera l'occasion de constituer, puis d'enrichir, une base de donnée avec l'ambition de structurer ces laboratoires en plateforme de R&D.

Paramagnetic properties of $[\text{An}^{\text{IV}}(\text{NO}_3)_6]^{2-}$ complexes (An = U, Np, Pu) probed by NMR spectroscopy and ab initio calculations.

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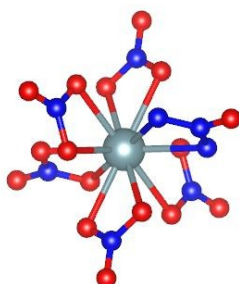
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Paramagnetic NMR measures the NMR chemical shift of paramagnetic complexes compared to their diamagnetic counterpart. This shift may be split into *dipolar* terms, arising from the magnetic dipolar interaction between the metal center and the NMR active nucleus, and the *contact* term, due to the spin delocalization leaking from the paramagnetic center towards the ligand [1]. The separation of these two contributions is often a bottleneck [2]. In this presentation, we will analyze the magnetic properties of three tetravalent actinide hexanitrate $[\text{An}^{\text{IV}}(\text{NO}_3)_6]^{2-}$ complexes with An = U, Np, Pu, (see Figure below) based on paramagnetic NMR and ab initio calculations. With pyritohedral symmetry (Th), the dipolar contribution is quenched by symmetry and consequently, the Actinide Induced Shifts (AIS) are from pure contact origin.

The AIS are calculated by quantum chemical tools, combining CAS based and DFT methods, in good agreement with the experimental values. There is an alternation of sign on the ligands due to spin polarization.

The hyperfine coupling (HFC) constants are deduced from the AIS and calculated by unrestricted DFT methods. The high symmetry and the simple structure of the ligands allow a decomposition of the HFC constants in terms of molecular orbitals contributions. This reveals the differential role of the core and valence orbitals depending on the position of the probed nucleus on the ligand and on the actinide cation, leading to information about the actinide-metal bonding scheme.



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SYNTHÈSE DE COMPLEXES DE LANTHANIDES DIVALENTS PAR ACTIVATION C–P SÉLECTIVE

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Les complexes sandwichs divalents volumineux de lanthanides suscitent actuellement un grand intérêt dans le domaine de la recherche scientifique eu égard à leur stabilité, leur réactivité et leurs propriétés physiques incontournables.^[1] Les ligands à base de polyarylcyclopentadiényle semblent des candidats très prometteurs dans la synthèse de ce type de structures, en raison de leurs propriétés stériques et électroniques stabilisantes.^[2] D'autre part, des substituants sur les aryles peuvent être facilement introduits lors de la synthèse du ligand, ce qui permet d'améliorer la solubilité des complexes et d'influencer ses paramètres électroniques. Récemment, nous avons rapporté une voie de simple de formation des complexes de lanthanide divalents (Sm, Eu, Yb) à partir du pentaphénylcyclopentadiène portant un groupement partant (GP) de type PPh₂ par clivage sélectif de la liaison C(Cp)–P.^[3] Afin d'explorer les potentialités de cette méthode, nous nous sommes intéressés à étendre son champ d'application à l'utilisation d'autres pro-ligands, en particulier C₅Ph₅P(O)Ph₂ et C₅Ph₅P(S)Ph₂. Nous allons également présenter des aspects mécanistiques de ces transformations.

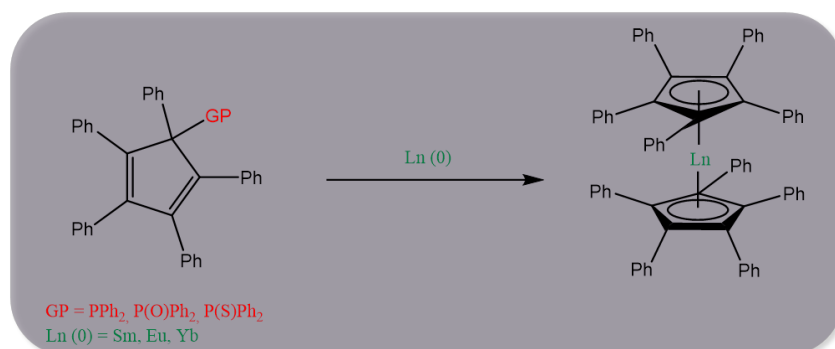


Schéma 1 : Synthèse des complexes sandwichs divalents par activation C-P sélective

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NEW INSIGHT IN LANTHANIDE PHOTOPHYSICS THANKS TO TRANSIENT ABSORPTION SPECTROSCOPY

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Luminescent lanthanide complexes find broad application in UC processes and beyond: in lasers or displays, in solar cells, as anti-counterfeit materials, in photocatalysis and particularly as bioprobes in photodynamic therapy or imaging. Owing to the particular nature of the 4f-electrons, the photophysical properties of f-element are unique (parity-forbidden f-f transition, sharp transition, long lifetime and low absorption coefficient). Due to the abovementioned parity-forbidden transitions, direct population of the lanthanides' excited state is quite inefficient. As an alternative to the use of very powerful excitation sources this issue can be addressed more elegantly by indirect population of the emitting states using sensitizing chromophores. This so-called "antenna effect" relies on the excitation of the chromophore, followed by an energy transfer from its singlet or triplet state to the lanthanide, which then relaxes back to its ground state by emitting sensitized light. In this contribution, we will show through selected examples that transient absorption spectroscopy in the ns- μ s regime is a powerful tool to shed light on the photophysical pathways beyond the "antenna effect". Particular attention will be devoted on the role of oxygen as triplet excited state quencher.

Références

FROM SWITCHABLE NANOMAGNETS TO MAGNETIC DENDRIMERS

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High spin molecules and photomagnetic compounds are attracting increasing attention due to their potential interest in memory devices or optical switches.¹ On the one hand, lanthanides have been recognized as viable building blocks for single molecule magnets (SMM) due to their strong single-ion anisotropy. On the other hand, octacyanometalates could be considered as interesting precursors not only for the drastic increase of their magnetization induced by visible light irradiation, but also for the design and synthesis of multicomponent architectures.²

In this presentation, we focus on three topics that emerge from our research:

- High spin molecules based on polycyanometallates precursors and magnetic dendrimers viewed as promising nanomagnets.³
- A family of photo switchable compounds, fully characterized by several techniques (XRD, SQUID, EPR, XMCD, ...) in order to well understand the photo-magnetic processes that might vary from one compound to the others (spin transition, electron transfer, bond breaking).⁴⁻⁶
- The design and the synthesis of hetero-tetra-metallic complexes, combining up to four different metallic ions in order to combine multi-properties, with the potential of featuring luminescent, magnetic and photo-switching properties (fig. 1).⁷

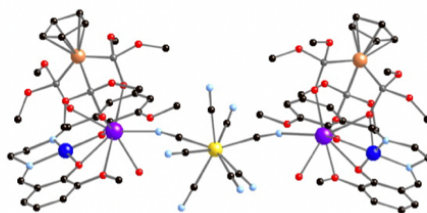


Fig. 1 The hetero-tetra-metallic complex: Mo(TbCuCo)₂ (example of a multifunctional nanomagnet)

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ADVANCED BIOIMAGING: IMPROVED LANTHANIDE LUMINESCENT BIOPROBES THROUGH PYCLEN REGIOFUNCTIONALIZATION

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Lanthanide Luminescent Bioprobes (LLBs) exploit the peculiar properties of lanthanides such as sharp and intense emission band spread from the visible to the Near Infra-Red (NIR) and long luminescent lifetimes (up to ms for Eu and Tb), which make them useful tools for time-resolved optical imaging.¹ Structurally, LLBs consist in lanthanide chelates functionalized with a chromophore in charge of sensitizing the metal centre. Polyazacycloalcanes are well known to form highly stable metal complexes. Among them, due to the rigidity brought by its pyridine unit, pyclen has emerged as an interesting platform and was studied in our group to develop Lanthanide (Ln³⁺) complexes with great photophysical properties under one-photon excitation.² However, UV-excitation limits the potential of these bioprobes because of its poor penetration in tissues. We will present here the conception of new generations of LLBs (Figure 1) exploiting the advantages of two-photon excitation (biological transparency windows, high resolution). Indeed, functionalization of pyclen with π -conjugated antennas led to LLBs with astonishing emissive properties.³ Cell imaging was successful thanks to the high brightness of the bioprobes, even with both excitation and detection in the NIR channel. Imaging studies performed on Zebrafish also demonstrated the potential of these LLBs for *in vivo* imaging. We then confirmed that the introduction of a coupling function on the pyclen skeleton for further targeting preserves the photophysical properties of the bioprobes.⁴

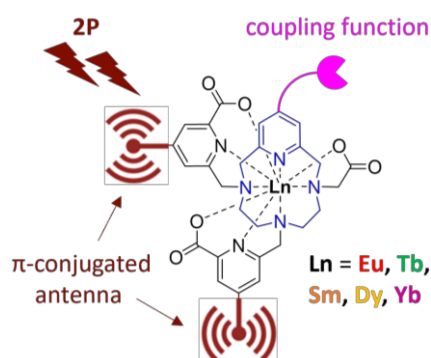


Figure 1 : General structure of the pyclen complexes developed.

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IMPACT OF A SOFT S-DONOR ATOM ON LUMINESCENT SINGLE-MOLECULE MAGNETS

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The field of molecular magnetism has witnessed remarkable progress in the last decades, fuelled by the discovery of single-molecule magnets (SMMs).^[1,2,3] Research into SMMs in the decades that followed saw the introduction of lanthanide ions into these complexes thanks to their high spin and strong intrinsic magnetic anisotropy.^[4,5] Some lanthanide ions also have very specific optical properties. As *f-f* transitions are forbidden by Laporte's rule, their absorption and emission bands are thin, and their lifetimes are long. Among the diverse elements employed as ligands in SMMs, sulphur stands out as a particularly intriguing coordinating atom due to its soft-donor character and its potential to impact both the magnetic and luminescent properties of metal complexes.^[6] The aim of this work is to develop new SMMs complexes based on Ln³⁺ ions and β -thioketonate ligands, and the study of the correlation between their structures and properties.^[7] A new family of Ln³⁺ (Tb³⁺, Dy³⁺, Er³⁺, Yb³⁺) mononuclear complexes based on β -thioketonate ligands has been isolated as single crystals. Magnetic and photophysical properties of a complex have been studied and rationalized by *ab initio* calculations to illustrate the correlation between the metal-ion environment and their SMM behaviours (Figure 1).

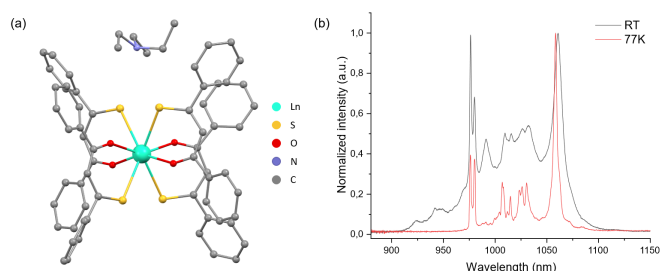


Figure 1 Cristal structure of (Et₃NH)[Ln(L)₄] (L = 1,3-diphenyl-3-thioxopropan-1-one). H-atoms removed for clarity (a). Room and low temperature solid-state emission spectra of (Et₃NH)[Yb(L)₄] under irradiation at $\lambda_{\text{exc}} = 413$ nm (b).

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VERS LE DÉCRYPTAGE DES ÉTAPES DE NUCLÉATION ET CROISSANCE DES NANOPARTICULES COLLOÏDALES DE PuO₂

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Une meilleure compréhension des propriétés structurales et physico-chimiques des nanoparticules colloïdales d'oxyde de plutonium (PuO₂) suscite un intérêt pour élucider les schémas de migration environnementale de cet élément radioactif à vie longue, mais aussi pour le développement potentiel de combustibles nucléaires avancés.[1,2] Les suspensions colloïdales issues de l'hydrolyse de Pu(IV) sont désormais décrites comme des nanoparticules cristallines de PuO₂ mesurant environ 2 nm de diamètre et présentant un désordre structural lié à un effet de surface.[3] Bien qu'un cluster hexamérique de Pu(IV) ait été récemment observé en tant qu'intermédiaire réactionnel lors de la formation de ces dernières, des questionnements subsistent quant à leur mécanisme général de formation.[4] La diffusion (SAXS) et l'absorption (XAS : XANES/EXAFS) des rayons X sur synchrotron semblent particulièrement adaptées à la mesure des variations de morphologie et d'environnement atomique ayant lieu lors de la nucléation et de la croissance des nanoparticules colloïdales de PuO₂. Afin de suivre l'hydrolyse du Pu sur la ligne MARS du synchrotron SOLEIL, un module de chauffe (Figure 1) répondant au cahier des charges de l'installation pour la manipulation d'échantillons radioactifs en température, a été développé. Le suivi cinétique de l'hydrolyse du Pu pourra alors être suivi par décomposition thermique d'un agent complexant stabilisant le Pu(IV). Les essais préliminaires ont permis de démontrer la faisabilité de cette approche au cours de laquelle la dégradation d'un peroxyde de Pu(IV) et la formation de colloïdes de Pu(IV) qui en résulte ont pu être observées par spectroscopie d'absorption dans le visible.

Par ailleurs, le module de chauffe a été testé préalablement sur un système analogue dans lequel le zirconium est utilisé comme substitut du Pu. Les premiers résultats ont confirmé que le zirconium peut être protégé de l'hydrolyse par sa complexation avec H₂O₂, et que la chauffe de ce système chimique permet de déclencher la formation de colloïdes de Zr. Cette présentation permettra de présenter les avancées sur ce projet en discutant des étapes qui ont été nécessaires au développement du module de chauffe ainsi que les résultats préliminaires obtenus avec Pu et Zr.



Figure 1 : Photographie du module de chauffe

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NMR PARAMAGNETIC EFFECTS OF LANTHANIDE COMPLEXES
UNDER HIGH HYDROSTATIC PRESSURE TO PROBE THE
STRUCTURE OF PROTEINS AND CONTRAST AGENTS.

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The application of hydrostatic high-pressure (HP) is now a recognized tool to modify biomolecular conformational landscapes in a mild and largely reversible manner. HP combined with NMR spectroscopy (HP-NMR) has been extensively used over the years to characterize the folding properties and the dynamics of soluble proteins by stabilizing conformational states that are lowly populated at ambient pressure and characterized by lower partial volumes. On the other side, paramagnetic NMR is a well-established method to probe the molecular structure by grafting compounds, such as lanthanides, on proteins and is also central for the development of contrast agents used for MRI. As an example, the Pseudo-Contact Shifts (PCSs) generated by lanthanides such as Yb³⁺, Tb³⁺ or Tm³⁺ lead to spectral shifts allowing obtaining precise relative positions of the various atoms with respect to the lanthanide probe. Nevertheless, to date, how pressure affects the paramagnetic properties of lanthanides and whether PCS can be used to probe protein structure/dynamics at high pressure is unknown.

Here, we will describe recent progress to assess the pressure effects on PCS collected on ubiquitin protein and a contrast agent. We show that up to 2500 bars, the paramagnetic probe remains chemically intact and that the change in paramagnetic susceptibility tensor is significant but limited. We could detect at ultra-high precision the minute conformational deformation of the contrast agent by a fraction (~1%) of Å. Using Tb³⁺ and Tm³⁺ grafted at various positions on ubiquitin we could detect high quality PCSs for backbone ¹H/¹⁵N atoms from 1 to 2500 bars. We detected a small displacement (~0.5 Å) of the probe from the protein at high pressure and demonstrated that PCSs can be used to probe the structure/dynamics of proteins under high-pressure conditions. Taken together, we established that paramagnetic NMR is a viable tool to characterize molecular structures under high pressure.

EXPLORING THE REACTIVITY OF YTTERBIUM – STABILIZED Pd^{IV} ALKYL SPECIES

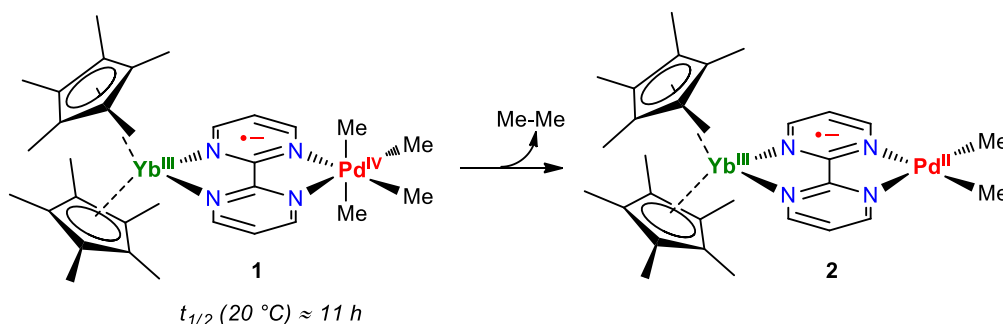
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Palladium-mediated transformations are dominated by Pd⁰ and Pd^{II} species, whereas the reactivity of higher oxidation states such as Pd^{III} and Pd^{IV} are far less explored because of the low accessibility and stability of these species. [1]

Herein, we present the synthesis, characterization, and reactivity of a novel Pd^{IV} - alkyl complex. The stabilization of the Pd^{IV} species through the Yb – bipyrimidine fragment [2, 3] gives rise to a complex (**1**) considerably more stable than its precursors ($t_{1/2} \approx 11$ h, 20°C) allowing the study of its reactivity. The obtained results contribute to a better understanding of the reactivity of high-oxidation states Pd species showing their possible applications in redox transformations. We are particularly interested in the photochemistry of the stable Pd^{IV} species and several examples will be presented.



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ABOUT THE ASSESSMENT OF THE CIRCULARLY POLARIZED LUMINESCENCE OF LANTHANIDE COMPLEXES

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Recent years have seen a renewed interest in circularly polarized luminescence (CPL), the emission asymmetry observed with luminescent chiral molecules. These studies are driven by potential applications, such as bioprobes for microscopy or optimized dyes for current displays, and by the widespread availability of CPL spectrophotometers. While chiral lanthanide(III) complexes are considered the most promising emitters, displaying record dissymmetry factors (g_{lum}) and good quantum yields, there is a need for fundamental studies on model compounds to determine the impact of the chemical structure and experimental conditions on the observed CPL properties.

In recent years, a collaborative effort involving molecular engineering, computational chemistry and instrumental development has allowed us to obtain first results on a series of helical Ln(III) complex.^{1,2} Our studies have highlighted the influence of temperature and spectrometer parameters on the measured g_{lum} .^{3,4} We think these results should prompt our community to reevaluate the procedures and the metrics used to quantify the performance of Ln complexes among other CPL emitters.

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IS RADIOCHEMISTRY REAL COORDINATION CHEMISTRY?

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Since the discovery and early developments of radiochemistry by P. and M. Curie at the beginning of the XXth century, the chemistry of radioactive nuclides has undergone spectacular progresses during the first half of the century. Since then the term *radiochemistry* broadly covers the chemistry at tracer scale from early Curie's methodologies¹ and the chemistry of radionuclides. The IUPAC gold book quotes "radiochemistry, that part of chemistry which deals with radioactive materials. It includes the production of radionuclides and their compounds by processing irradiated materials or naturally occurring radioactive materials, the application of chemical techniques to nuclear studies, and the application of radioactivity to the investigation of chemical, biochemical or biomedical problems."²

After the discovery of Pu in 1940³, the concept of actinide series was proposed by G. T. Seaborg.⁴ According to Seaborg's early views, the radioelements starting at Ac (to Lr) belong to the so called actinide series (also called 5-*f* series), which himself belongs to a subgroup of the transition metal series.⁵ Very soon, chemists started to develop the coordination chemistry of the actinide elements and compared it to that of transition metals. But from the IUPAC definition, fundamental coordination chemistry of the actinide elements does not obviously fall into the definition of *radiochemistry*.

From an epistemological point of view, should *radiochemistry* be considered as part of the transition metal coordination chemistry? Or from historical reasons, should *radiochemistry* have a rather more restrictive definition? What are the connections and disconnections between *radiochemistry* and coordination chemistry?

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ACTINIDE XAS STUDIES AT THE MARS BEAMLINE OF SOLEIL

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MARS (Multi-Analyses on Radioactive Samples) beamline at the SOLEIL synchrotron is opened to the international community since 2010 and is dedicated to the study of radioactive samples [1] with a specific radioprotection safety design that fulfills the French ASN (Autorité de Sûreté Nucléaire) requirements. The beamline is fully devoted to advanced structural and chemical characterizations of radioactive matter, in particular actinides, using hard X-rays in the 3-35keV energy range. Today, the maximum radioactivity allowed on the beamline, including the storage, is 185 GBq with a maximum of 18.5 GBq per sample. Currently, different types of experiments are available: standard and high-resolution X-ray absorption spectroscopy (XAS) [2,3], transmission X-ray diffraction (TXRD), high-resolution X-ray diffraction (HR-XRD) [4], and associated X-ray microbeam techniques (μ XRF/ μ XRD/ μ XAS). Small angle and wide angle X-ray scattering (SAXS/WAXS) are also available.[5]

This contribution presents the status of the beamline and a selection of XAS studies on actinides related to the biological and environmental field.

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LISTE DES POSTERS

P01	Complexation du protactinium(V) en solution aqueuse	Claire LE NAOUR
P02	Original Photoactive Cerium-Based Catalyst for Photoinduced Electron Transfer	Adrien COMBOURIEU
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COMPLEXATION DU PROTACTINIUM(V) EN SOLUTION AQUEUSE

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Le protactinium connaît actuellement un regain d'intérêt en raison d'une application potentielle dans différents domaines en marge du nucléaire civil (réacteur à combustible thorium, accumulation de ²³¹Pa dans les résidus miniers d'uranium) : détermination du rapport ²³¹Pa/²³⁰Th en océanographie et du rapport ²³¹Pa/²³⁵U en criminalistique nucléaire ou géochronologie, irradiation de ²³¹Pa ou ²³²Th pour la production de ²³⁰U à des fins médicales (thérapie alpha ciblée). Quelle que soit l'application, une meilleure connaissance des propriétés chimiques de cet élément est requise.[1]

Le protactinium au degré d'oxydation (V) se différencie des actinides du début de la série par l'absence de liaison di-oxo dans ses composés en phase condensée : seule la présence d'une liaison mono-oxo courte a été mise en évidence dans les milieux oxalique et sulfurique, alors que de purs fluoro complexes sont observés en milieu HF.[2] Cette particularité reste mal comprise à l'heure actuelle.

Nous présentons ici la démarche adoptée pour l'étude de la complexation de Pa(V) en solution aqueuse en l'illustrant par quelques exemples. Des constantes de complexation sont déduites d'expériences d'extraction liquide-liquide combinée à la spectrométrie gamma. Dans ce cas, l'élément est à l'échelle des ultra-traces ce qui permet de s'affranchir des phénomènes de polymérisation mais seules des compositions moyennes de complexes sont obtenues. L'étude thermodynamique est complétée par une étude spectroscopique par IR et absorption X avec le Pa à l'échelle millimolaire en présence d'un complexant fort ou/et d'une acidité élevée pour limiter l'hydrolyse et la formation de colloïdes.

Des calculs théoriques sont également réalisés afin de caractériser l'environnement de coordination du cation avec les ligands et les molécules d'eau, et de déterminer la stabilité relative des complexes formés. [3] Les structures obtenues sont alors utilisées pour ajuster les oscillations EXAFS.

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ORIGINAL PHOTOACTIVE CERIUM-BASED CATALYST FOR PHOTOINDUCED ELECTRON TRANSFER

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Catalysis is a fascinating opportunity for chemists to unbolt new reaction pathways in mild conditions. Among promising fields of catalysis, photoredox catalysts have shown good reactivity. However, mostly-used photocatalysts are still mainly based on precious metals such as iridium and ruthenium. Efforts to develop more abundant metals photoactive complexes brought some examples using iron, copper, and chromium complexes as photocatalysts. However, they remain only mildly reductive. Among other abundant metals, cerium is an interesting candidate: as abundant as cobalt (66.5 ppm) and cheaper, its comprehensive photochemical behaviour has been recently highlighted both as a powerful Single-Electron Transfer (SET) reagent in +III oxidation state,^{1,2} and as a Hydrogen Atom Transfer (HAT) reagent in +IV oxidation state, even capable of activating light alkanes (including methane).^{3,4}

Nevertheless, the widespread use of CeCl_3 as the photocatalyst hampers the progress in cerium photocatalysis. Indeed, its low solubility in apolar solvents significantly narrows the scope of possible reactions in mild conditions, and non-tunable redox potential complicates using this species in a multicatalytic system. Moreover, the mechanism of HAT reactions of cerium is still discussed, mainly the nature of the HAT agent. This is particularly due to the high coordination number of lanthanide complexes, which renders the intermediates more difficult to ascertain.

To overcome those issues, we synthesized a highly soluble cerium complex: $\text{Ce}(\text{N}(\text{CH}_2\text{CH}_2\text{NSi}^i\text{Pr}_3)_3)$ $\text{CeTREN}^{\text{TIPS}}$, which displays SET reactivity with aryl and alkyl halides (Cl, Br, I) under +III oxidation state. Having a single open apical coordination position, $\text{Ce}^{\text{III}}\text{TREN}^{\text{TIPS}}$ can be easily oxidized in corresponding Ce^{IV} mono-halides.

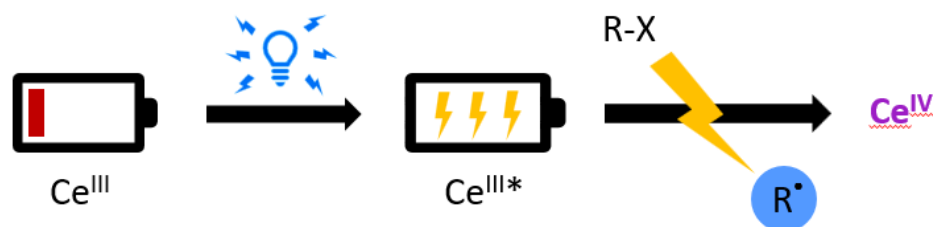


Figure 1 - $\text{Ce}^{\text{III}}\text{TREN}^{\text{TIPS}}$ SET reactivity

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PHOTOCATALYTIC PRODUCTION OF GREEN HYDROGEN FROM DISTILLERY WASTES

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The transition from the exploitation of fossil fuels to the efficient use of sustainable energies is the main goal of the researchers of the 21st century. Hydrogen has emerged as a clean fuel alternative to fossil energies, due to its absence of carbon dioxide emission when used. [1]

However, the production of green hydrogen has been very challenging and is today a focus of the scientific community. Photocatalytic processes have been promising, giving the possibility to harness sunlight energy to produce hydrogen from water splitting. [2]

This project aims to couple this photocatalytic production of H₂ to the photodegradation of distillery wastes, which can be considered as an inexpensive, locally sourced, and available resource. Giving the possibility to distilleries to produce energy from their wastes could help them achieve energy autonomy and reduce their environmental impact.

The hydrogen production is carried out by a highly active cadmium sulfide quantum dots (CdS QDs) photocatalyst, using the alcoholic wastes as sacrificial agents. Parameters of the CdS QDs synthesis have been optimized to improve their reactivity for methanol degradation (model alcohol) and real industry wastes.

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PHOTOINDUCED ISOMERIZATION OF CYCLONONATETRAENYL ANION LIGAND IN LANTHANIDE SANDWICH COMPLEXES

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The cyclonatetraenyl (Cnt) anion is nine-membered ring that was first synthesized in 1963 by Katz and Garrat.¹ This compound features two isomers: the *cis,cis,cis,cis*-Cnt and the *cis,cis,cis,trans*-Cnt as depicted in Figure 1. At that time, scientists observed spontaneous isomerization from the *trans* form to the *cis* one. Given the aromatic character of the fully *cis* form, it was considered the stable form of the two and quite logically the system was evolving toward stability. Unfortunately, the high sensitivity of the Cnt⁻ ligand, toward protonation and reorganization into 8,9-dihydroindene precluded further analysis.

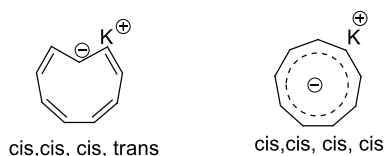


Figure 1: Cyclonatetraenyl anion isomers

Despite all these challenges, the Cnt ligand has regained interest in organometallic chemistry to form sandwich complexes.^{2,3} Our group has expanded this result to a series of lanthanide-containing complexes, where it was shown that a mixture of the *cis* and *trans* isomer complexes were observed.⁴ After careful evaluation of the different stimuli that could cause such species to be isolated, we come to the conclusion that in certain cases the isomerization is photo-induced. Thus, this work focuses on how to control the isomerization of the Cnt⁻ ligand and its complexes using light.

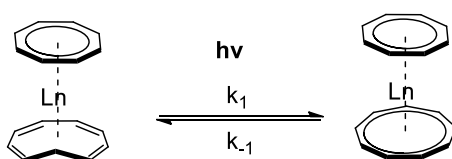


Figure 2: Photoinduced isomerization of Cnt in lanthanide complexes

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CO REDUCTIVE COUPLING ON Tm^{II} AND FUNCTIONALISATION
WITH CO_2 AND OTHER $C=O$ COMPOUNDS

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Divalent lanthanide (Ln^{II}) complexes are attractive single-electron reductants as their reactivity can be tuned by the nature of both the Ln^{II} metal centre and the ligand. In this context, Ln^{II} complexes have been actively investigated for the activation and transformation of small molecules. In particular, homogeneous complexes allowing the activation and valorisation of CO under mild conditions are highly desirable. To date, only a limited number of systems has been able to promote the reductive coupling of CO molecules, and includes a handful of low-valent f block complexes.^[1] For example, the well-studied divalent samarium complex $[Cp^*_2Sm(THF)_2]$ mediates CO reductive trimerisation.^[2]

Using a highly reductive and sterically hindered Tm^{II} complex, selective CO reductive dimerisation or trimerisation was achieved depending on the experimental conditions.^[3] Further functionalisation reactions were performed using CO_2 (see Figure below) and other $C=O$ electrophiles, resulting in the formation of novel oxygenated multicarbon products,^[3] as well as original cycloaddition products.^[4]

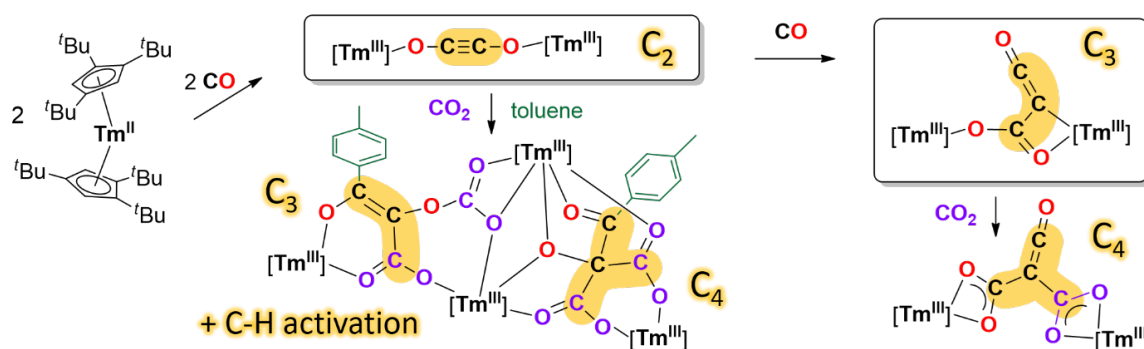


Figure: Activation of CO by a Tm^{II} complex and further reactivity upon addition of CO_2 .

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YTTERBIUM STABILIZED ALKYL PALLADIUM(IV) COMPLEXES:
SYNTHESIS AND REACTIVITY STUDIES

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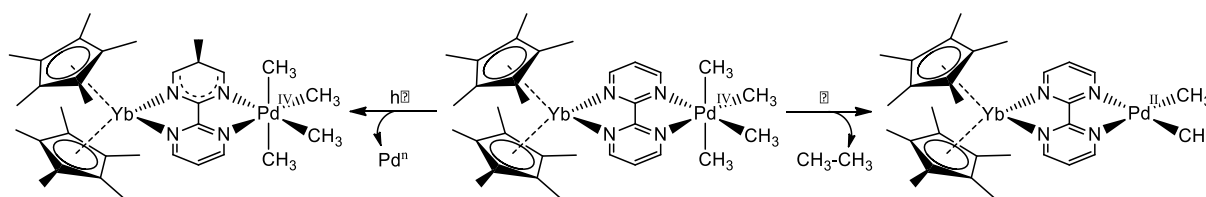
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The chemistry of organometallic palladium complexes is largely dominated by the 0 and +II metal's oxidation states due to their central relevance in cross-coupling transformations.[1] However, higher oxidation states of the metal are being explored in the effort to access previously precluded transformations and to unveil unprecedented reactivity at the metal centre.[2,3]

The coordination of an ytterbium centre to an alkyl-Pd^{IV} species through a redox non-innocent ligand dramatically improves the stability of the resulting complexes.[4,5] However, owing to the presence of labile ligands as halides, such compounds are still susceptible to undergo easy R.E. processes.[4]

Following this effort, here we present the synthesis of an ytterbium-stabilized alkyl-Pd^{IV} species bearing four methyl groups at the palladium centre. Such complex proved to be dramatically more stable than its tris-methylated counterparts, with a half-life time in solution of 11 hours at 20°C. Taking full advantage of the increased lifespan in solution of the resulting complex, its unprecedented reactivity with light is explored.



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X-RAY STRUCTURES AND MAGNETIC PROPERTIES OF COORDINATION DENDRIMERS

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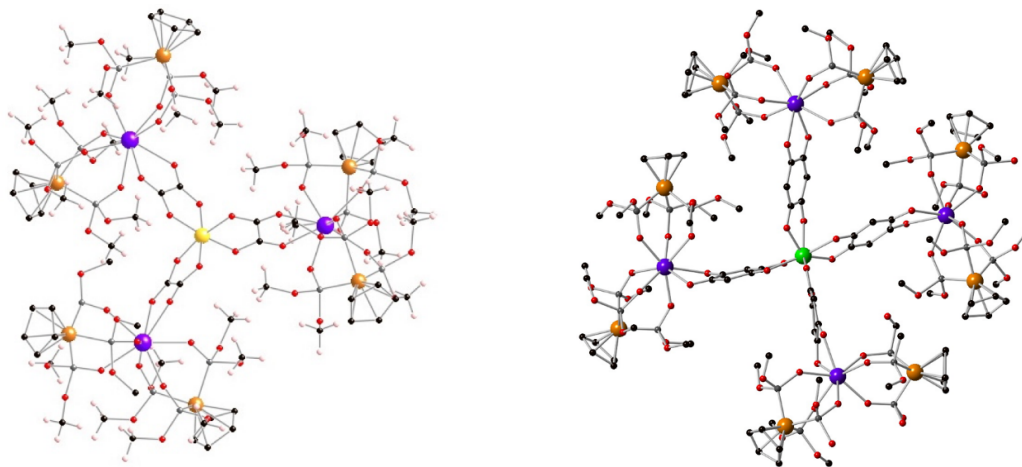
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Résumé: Developed in the 1980s, dendrimer chemistry has opened up new perspectives in fields as diverse as catalysis, molecular electronics and artificial photosynthesis.[1] Surprisingly, however, magnetic dendrimers are not common in the literature due to puzzling difficulties in their synthesis and characterization.[2] In this context, the design of such multimetallic and monodisperse starburst architectures, endowed with magnetic properties, is therefore a real challenge.[3]

Following a supramolecular “complex as ligand” approach, we succeeded in this challenge by carrying out the synthesis, characterization (including X-Ray diffraction) and study of magnetic dendrimers. Our synthetic strategy essentially relies on (i) oxalate-based coordination chemistry as the core of the architecture and (ii) trinuclear complexes, LnCo₂ for the branches (with Ln a lanthanide and Co, the Klaui ligand) that feature single-molecule magnet properties. The combination of these two building blocks allows us to obtain supramolecular and dendritic assemblies.

The versatility of this approach makes it possible to anticipate the properties according to the choice of metal cations involved in the structure (single molecule magnets or giant spin values, etc.). Thus we obtained hetero-tri-metallic magnetic dendrimers, MLn₃Co₆ and ZrLn₄Co₈ (with M=Co or Cr, and Ln=La, Tb, Dy, Er, ...) fully characterized by X-ray diffraction.[3] The magnetic properties are in good agreement with the expected theoretical models. This type of compound could be of great interest for applications in information storage or magnetic refrigeration.



Références :

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